ESD-TR-77-358

LEVEL II

Semiannual Technical Summary

Enhanced Heteroepitaxy

31 December 1977

Prepared for the Defense Advanced Research Projects Agency
under Electronic Systems Division Contract F19628-78-C-0002 by

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LEXINGTON, MASSACHUSETTS

Approved for public release; distribution unlimited.

78 07 31 166

The work reported in this document was performed at Lincoln Laboratory, a center for research operated by Massachusetts Institute of Technology. This work was sponsored by the Defense Advanced Research Projects Agency under Air Force Contract F19628-78-C-0002 (ARPA Order 3336).

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

Raymond L. Loiselle

Raymond L. Loiselle, Lt. Col., USAF
Chief, ESD Lincoln Laboratory Project Office

(11)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
LINCOLN LABORATORY

ENHANCED HETEROEPITAXY

SEMIANNUAL TECHNICAL SUMMARY REPORT
TO THE
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

1 JULY – 31 DECEMBER 1977

ISSUED 13 JUNE 1978

LEXINGTON MASSACHUSETTS

ABSTRACT

Oriented crystal growth on an amorphous substrate has been achieved using an artificially created submicrometer-dimension surface-relief grating. Crystallites of KCl grown from a water solution onto a 320-nm spatial-period square-wave grating in SiO_2 nucleated preferentially at vertical steps and grew with ⟨100⟩ directions parallel to the grating axis. 320-nm spatial-period square-wave gratings fabricated on amorphous SiO_2 substrates were used to produce uniform alignment of the director in nematic and smectic liquid-crystal layers. This demonstrates that molecular alignment can be achieved using surface structures fabricated by a planar process. A novel method of producing twisted-nematic liquid-crystal displays using surface gratings is described.

CONTENTS

INTRODUCTION

The objectives of this research program during calendar year 1977 are to:

(1) Determine the feasibility of using submicrometer-dimension surface-relief structures to control the orientation of a variety of deposited thin films,

(2) Determine if single-crystal films of low defect density can be produced using artificial surface-relief structures, and

(3) Determine if device quality AlN or ZnO films can be produced on SiO_2 or Si_3N_4 over Si.

The tasks within this program include: (1) the development of a technology for fabricating the required submicrometer surface-relief structures, (2) the deposition of thin film material, and (3) the analysis of structures fabricated and their influence on thin film growth and orientation.

This report consists of two parts that describe progress on task (2) in the second half of calendar year 1977. The feasibility of using submicrometer-dimension surface-relief structures, such as gratings and grids, to control the orientation of deposited thin films [objective (1) of this research program] has been demonstrated for KCl on amorphous SiO_2 and for nematic and smectic liquid crystals on the same substrates.

ENHANCED HETEROEPITAXY

I. ORIENTED CRYSTAL GROWTH ON AMORPHOUS SUBSTRATES USING ARTIFICIAL SURFACE-RELIEF GRATINGS

The nucleation and growth of crystalline overlayers are influenced by accidental structural features on a substrate surface, such as cleavage steps, scratches, pits, etc.[1,2] The influence of such structural features on overlayer properties has always been considered detrimental and, thus, workers have generally tried to achieve totally smooth substrate surfaces. We propose that artificially created surface microstructures might be employed to manipulate the growth and orientation of crystalline overlayers. One outcome of this approach might be a method of obtaining oriented crystalline films on substrates and under growth conditions that otherwise yield polycrystalline films. As an example of this, we demonstrate that a 320-nm spatial-period surface-relief grating etched into amorphous SiO_2 induces an orientation in KCl crystallites grown from a water solution.

Figure 1 is a scanning-transmission-electron micrograph showing the KCl crystallites after growth on a surface-relief grating in amorphous SiO_2. The sides of nearly all the rectangular KCl crystallites are aligned parallel and perpendicular to the surface grating. The smaller crystallites are generally located in grooves (the lighter shaded stripes), and it appears that growth is initiated at vertical steps. Selected-area electron diffraction patterns taken in a scanning-transmission-electron microscope (STEM) confirm one's intuition that the $\langle 100 \rangle$ directions are parallel to the sides of the crystallites. Clearly, the artificially imposed surface-relief grating has induced an oriented crystal growth. In areas of the SiO_2 surface where no surface grating is present, crystallite habit (i.e., shape) is found to be less regular, and $\langle 100 \rangle$ directions show no preferential azimuthal orientation. These results are the first demonstration of crystal orientation using artificial surface microstructures and are also a clear demonstration of oriented crystal growth (i.e., heteroepitaxy) on an amorphous substrate.

Our SiO_2 substrates were films, about 100 nm thick, grown by a commercial chemical-vapor-deposition (CVD) process over a 100-nm-thick Si_3N_4 film, also grown by a commercial CVD process, on a silicon wafer. Details of the techniques used to create the relief grating in SiO_2 are given elsewhere.[3,4] In brief, a grating was exposed in polymethyl methacrylate (PMMA) using Cu_L x-ray lithography. After development, a 10-nm layer of chromium was evaporated over the structure and a chromium grating was produced by liftoff. The SiO_2 was then etched in CHF_3 by reactive ion etching using the chromium grating as a mask. Finally, the chromium was removed in a chemical etchant. This procedure yields relief gratings having flat tops and flat groove bottoms and sidewalls that deviate a maximum of about 6° from the vertical. The radii of curvature at the corners where the sidewalls join the tops and the groove bottoms are less than 5 nm. The depth of the gratings used in the KCl experiments ranged from 25 to 50 nm. After producing the surface-relief grating, the silicon underlying the Si_3N_4 and SiO_2 films was etched away using ethylene diamine pyrocatechol in water.[5] The sample was held in a special fixture to avoid any etching of the front surface. The KCl was grown by flooding the SiO_2 grating with a solution of KCl in water and then blowing nitrogen gas over it to promote evaporation, supersaturation, and crystal growth. Crystal orientation in the grating area was uncorrelated with the blowing direction. Because our SiO_2/Si_3N_4 substrates were only about 200 nm thick, they

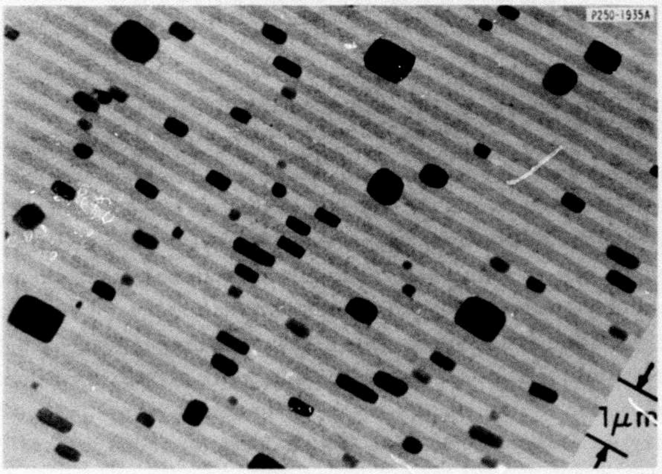

Fig. 1. Scanning-transmission-electron micrograph of KCl crystallites grown on a 320-nm spatial-period square-wave surface-relief grating in amorphous SiO_2 showing that the grating has induced an oriented crystal growth where ⟨100⟩ directions are parallel to the grating grooves. The grooves are 25 nm deep and have the lighter shading. The electron microscopy produces some decomposition of the KCl crystallites during viewing, leading to the serrated edges of some of the crystallites.

could be viewed in transmission by electron microscopy using both conventional and STEM systems. The STEM permitted selected-area electron diffraction, although the signal-to-noise ratio was poor.

The results shown in Fig. 1 indicate that the surface-relief grating influences both the nucleation and the growth of the KCl. Nucleation appears to occur preferentially at vertical steps, and subsequent growth is constrained and aligned by the steps. Preferential nucleation at naturally occurring cleavage steps (usually called "decoration") has been observed for many crystalline film-substrate combinations including Au on NaCl (Ref. 6), Au on LiF (Ref. 7), Ag on NaCl (Ref. 8), Sn on NaCl (Ref. 9), Ag on mica,[8] and Au on graphite,[10] and has been explained qualitatively using classical nucleation theory, with the assumption of isotropic surface tensions.[7] On the basis of this simplified theory, one can expect decoration of artificially created surface-relief steps on amorphous substrates if the radius of curvature at the base of the step is sufficiently small compared to the size of the critical nucleus, and if the contact angle of the deposit is <100°. An extension of the theory predicts that KCl will decorate steps on SiO_2.

The grating's orienting influence on the KCl growth can be explained on the basis that oriented growth corresponds to a minimum free energy configuration. When grown on smooth amorphous substrates, most alkali halides, including KCl, form textured films with {100} planes parallel to the substrate surface,[11] indicating that surface free energy is minimum for this particular texture. Our surface-relief grating consists of flat tops, flat groove bottoms, and nearly vertical sidewalls, and thus a crystal would have a higher free energy if it grows misaligned relative to such a structure than if it grows aligned. Our method of growing the KCl by evaporation of a solution is far from an equilibrium process. However, the KCl deposit was "annealed" after growth by placing it in a humid atmosphere for a few minutes prior to storage in a dessicator. Because of the islands' small size, we feel this annealing was sufficient to establish equilibrium.

Many polycrystalline thin films exhibit a texture when deposited on smooth amorphous substrates such that the most densely packed planes are generally parallel to the substrate surface.[11] Our technique may be effective in inducing azimuthal alignment in such cases as well.

The above results are an example of how the growth and orientation of an overlayer can be manipulated by an artificially created microstructure on a substrate surface. Since the spatial period, symmetry, cross-sectional profile and overall pattern configuration of artificial microstructures are subject to one's control, and since many aspects of overlayer growth and orientation are affected by surface structure, manipulation using artificial microstructures may be of rather general applicability and contribute to both the technology and the basic science of overlayer growth. Precisely how growth might be manipulated for any given overlayer/substrate combination will depend on the geometry of the microstructure, the method and conditions of the deposition, and the detailed mechanisms of nucleation and growth.[12]

H. I. Smith
D. C. Flanders

II. ALIGNMENT OF LIQUID CRYSTALS USING SUBMICROMETER PERIODICITY GRATINGS

Several researchers have demonstrated that surfaces which have been made anisotropic by rubbing with abrasives,[13] by directed oblique evaporation of silicon monoxide,[14] or by dipping in surfactants[15] will align nematic liquid crystals. It is believed that such alignment minimizes the free energy associated with elastic deformation of the liquid crystal. In particular, if the long axes of the liquid-crystal molecules are constrained to lie in, or at a small tilt angle to, the plane of a smooth surface, then one expects a grating structure on that same surface to induce alignment of the nematic director along the groove direction. Berreman[16,17] has proposed a detailed model which supports this idea.

Oblique evaporation and rubbing techniques produce surfaces with a topography that is largely uncontrolled and, thus, is difficult to reproduce or quantify exactly. We demonstrate here that liquid crystals can be aligned on gratings whose topography is directly controlled. It is significant that the spatial-period of the gratings used was 320 nm, which is much larger than the size of the molecules ($\approx$2 nm) being aligned. We expect the forces which favor alignment to increase with gratings of higher spatial frequency.

The gratings for the following experiments were fabricated in SiO_2 by reactive ion etching in CHF_3 gas using a mask of 100-Å-thick chromium. The chromium grating was produced by a liftoff process from a grating pattern exposed in PMMA using Cu_L soft x-ray lithography.[3] Holographic lithography was used as the pattern generation step in producing the x-ray mask. The etch depth of our SiO_2 gratings was about 25 nm. Recent measurements in a transmission-electron microscope on gratings fabricated by this process indicate that the sidewalls are within 6° of the vertical, and that the radius of curvature at the top and bottom corners of the sidewalls is less than 5 nm. Gratings were fabricated over a 1.25- × 1.25-cm area on two highly polished fused quartz substrates.* The two substrates were assembled into a sandwich with 50-μm-thick Teflon spacers holding them apart, as shown in Fig. 2. The gratings were on the inside of the sandwich and faced each other with their groove directions parallel. A high degree of parallelism is easily obtained by first roughly aligning the gratings so that a beam of light incident on them is simultaneously diffracted from both gratings toward an observer; then, fine adjustments

* Optosil 2, Amersil, Inc.

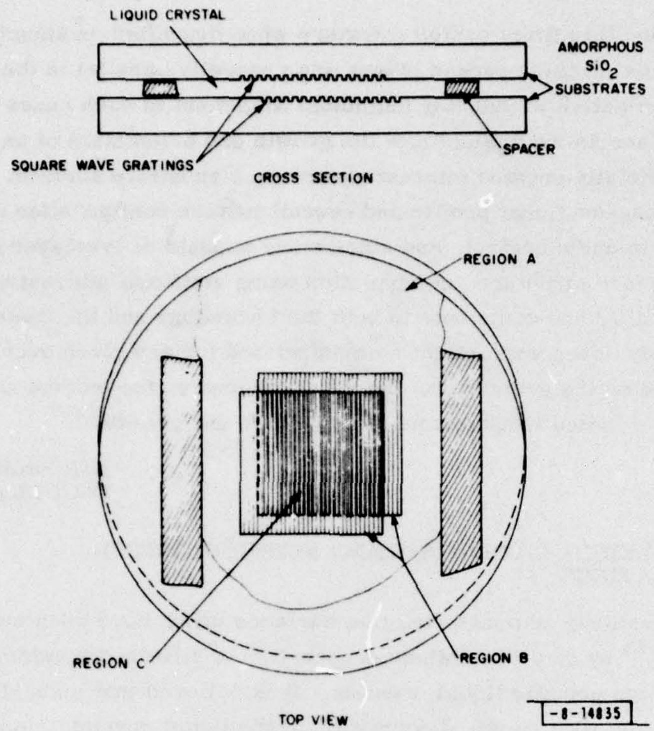

Fig. 2. A schematic cross section and top view of the "sandwich" assembly used to investigate surface-relief-structure orientation effects in nematic and smectic A liquid crystals. The two gratings are displaced relative to one another so that the effects of two facing gratings (Region C), a single grating (Region B), or no grating (Region A) can be compared.

in the alignment can be made while observing moiré interference fringe patterns in the overlapping diffracted beams.

After alignment of the gratings, the sandwich was heated above the nematic-isotropic transition temperature of MBBA [N-(p-methoxybenzilidene)-p-butylaniline] and the liquid crystal was introduced into the sandwich by capillary action. The sandwich was allowed to cool to room temperature where MBBA is nematic, and was observed in transmission in a microscope between crossed polarizers. The incident polarized light was normal to the thin liquid-crystal layer, and the entire sandwich could be rotated in the plane of the layer.

An aligned liquid crystal behaves as an optically uniaxial medium with its optic axis in the direction of the nematic director. When a linearly polarized beam of light is normally incident on a uniaxial slab of arbitrary thickness it will remain linearly polarized after passing through the medium only if the polarization is perpendicular to the optic axis or parallel to the projection of the optic axis on the slab. In the area between the two gratings, distinct peaks and nulls in the light transmission were observed as the sandwich was rotated, the nulls occurring every 90°. Furthermore, the entire liquid-crystal layer in the grating area had a uniform brightness, with nulls in the light transmission occurring simultaneously across the entire field of view. Our interpretation is that the nematic director is not perpendicular to the substrates and that it is uniformly oriented in the grating area. The liquid-crystal layer had a distinctly different appearance in the region outside the grating area where it was confined between two smooth surfaces. It did not appear uniform, and many small domains were visible indicating that the direction of the nematic director varies randomly in this region. The light transmission in the grating area went through a null when the incident polarization was along the groove direction, to within the experimental error of our apparatus (~0.5°). This indicates that the projection of the nematic director was aligned along the groove direction or perpendicular to it. In order to distinguish these two possibilities, we doped the MBBA with the dye DODCI (3, 3' diethyloxadicarbocyanine iodide), which aligns with the nematic director and absorbs most strongly light that is polarized in the direction of alignment. In this way, we established that the nematic director projection was along the groove direction.

The angle between the nematic director and the plane of the substrate was estimated by measuring the difference between the refractive index for the ordinary wave and the extraordinary wave with light normally incident on the substrate. The extraordinary index varies with the angle between the incident ray and the optic axis. To make the measurement, one of the Teflon spacers was removed, thereby introducing a known tilt between the two quartz substrates. When viewed at normal incidence in monochromatic light (589 nm) between crossed polarizers, distinct dark and light bands were visible due to the linear variation in thickness of the birefringent medium. The dark bands occur when the relative phase shift between ordinary and extraordinary waves is an integral number of cycles. Knowing the tilt between the two substrates, the difference in index of refraction can be calculated from the spacing of the bands.[19] We measured an index difference of 0.18 ± ~10 percent. This corresponds to a nominal tilt of 23° between the nematic director and the substrate plane; this was the same inside and outside the grating area. For the tilt calculation, we used the value of 0.225 (±0.006) for the birefringence of MBBA at 25°C, which is correct if the nematic-isotropic transition temperature is in the range of 41 to 45°C.[18] The transition temperature is sensitive to the purity of the liquid crystal and typically drops slowly when MBBA is first exposed to air, with a corresponding decrease in the birefringence. Though we did not measure it, the transition temperature is usually in the range of 41 to 45°C. Furthermore, conoscopic examination of our sample confirmed that the nematic director was tilted at least 20° from the substrate plane.

Surface contamination can make the nematic director approach the substrate normal and thus degrade the orienting influence of the grating. Freshly made substrates, and those cleaned in UV-generated ozone[19] or concentrated H_2SO_4, exhibited good alignment, low tilt angle, and consistent results. Both highly polished fused quartz and SiO_2 prepared by thermal oxidation of silicon wafers showed similar results.

We also aligned the liquid crystal M24 (BDH Chemicals Ltd., 4-cyano-4'-octoxybiphenyl), which has a smectic A as well as a nematic phase. We found that M24 in the nematic phase aligned uniformly along the groove direction in the grating area, but it exhibited a slowly varying nematic director outside the grating area where it was not constrained. The effect of the grating was striking when the liquid crystal was cooled to the smectic phase. The liquid crystal in the grating area appeared as a uniform uniaxial slab with the projection of its optic axis parallel to the groove direction; outside the grating area a multitude of striations and fan-shaped defects appeared. No striations were visible in the area confined between two gratings.

Based on the above results, we have constructed a novel type of twisted nematic display using grating technology. Gratings of 100-nm-thick gold lines and 320-nm period were fabricated on a 225-μm-thick Corning 0211 glass substrate using holographic lithography and ion-beam etching. The gold grating lines were interconnected by a continuous gold film which surrounded the grating area. Two of these 0211 glass pieces were assembled into a sandwich using

Teflon spacers to maintain a gap between them. The gratings, which were inside the sandwich, were oriented with their groove directions perpendicular to each other. Electrical contact was made to each gold surface. All the elements of a twisted-nematic display are present in this structure: (a) the gratings provide two liquid-crystal-aligning surfaces at right angles to one another, (b) the gratings polarize light and act as crossed polarizers, and (c) the gratings are highly conductive at DC and form effective conducting parallel plates to align the liquid crystal by means of an electric field. The contrast ratio of the polarizer limits the performance of the display. Contrast ratios of 10:1 have been obtained using He-Ne laser light (632.8 nm). Improvements should be obtained with gratings of finer spatial period.

In conclusion, we have demonstrated that square-wave-grating surface-relief structures can be used to align nematic and smectic liquid crystals. Since these structures are well controlled and characterized, they permit quantitative models for alignment of liquid crystals by surfaces to be tested. Finally, surface structures may find wide application in other systems where anisotropic surface interactions are present.

D. C. Flanders
D. C. Shaver
H. I. Smith

REFERENCES

1. K. L. Chopra, Thin Film Phenomena (McGraw-Hill, New York, 1969).
2. Handbook of Thin Film Technology, Chapters 8 and 10, edited by L. I. Maissel and R. Glang (McGraw-Hill, New York, 1970).
3. D. C. Flanders, H. I. Smith, H. W. Lehmann, R. Widmer, and D. C. Shaver, Appl. Phys. Lett. 32, 112 (1978).
4. D. C. Flanders and H. I. Smith, J. Vac. Sci. Technol. 15, No. 3 (May/June 1978).
5. J. C. Greenwood, J. Electrochem. Soc. 116, 1325 (1969); A. Bohg, J. Electrochem. Soc. 118, 401 (1971).
6. G. A. Bassett, Philos. Mag. 3, 1042 (1958).
7. B. K. Chakraverty and G. M. Pound, Acta Metall. 12, 851 (1964).
8. K. L. Chopra, J. Appl. Phys. 37, 3405 (1966).
9. G. Shimaoka and G. Komoriya, J. Vac. Sci. Technol. 7, 178 (1970).
10. G. R. Henning, Appl. Phys. Lett. 4, 52 (1964).
11. E. Bauer, Trans. 9th Vac. Sym. AVS, 1962, edited by G. H. Bancroft (Macmillan, New York, 1962), p. 35; E. Bauer, in Single Crystal Films, edited by M. H. Francombe and H. Sato (Pergamon Press, London, 1964), p. 43.
12. D. C. Flanders, PhD Thesis, February 1978, M.I.T. Department of Electrical Engineering and Computer Science.
13. L. T. Creagh and A. R. Kmetz, Mol. Cryst. Liq. Cryst. 24, 59 (1973).
14. J. L. Janning, Appl. Phys. Lett. 21, 173 (1972).
15. J. E. Proust, L. Ter-Minassian-Saraga, and E. Guyon, Solid State Commun. 11, 1227 (1972).
16. D. W. Berreman, Phys. Rev. Lett. 28, 1683 (1972).
17. ______________, Mol. Cryst. Liq. Cryst. 23, 215 (1974).
18. I. Haller, H. A. Huggins, and M. J. Freiser, Mol. Cryst. Liq. Cryst. 16, 53 (1972).
19. J. R. Vig, IEEE Trans. Parts, Hybrids and Packaging PHP-12, 365 (1976).

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER 18 19
ESD-TR-77-358

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER 9

4. TITLE (and Subtitle) 6
Enhanced Heteroepitaxy

5. TYPE OF REPORT & PERIOD COVERED
Semiannual Technical Summary rept.
1 July - 31 December 1977

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) 10
Alan L. McWhorter

8. CONTRACT OR GRANT NUMBER(s) 15
F19628-78-C-0002

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Lincoln Laboratory, M.I.T.
P.O. Box 73
Lexington, MA 02173

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
ARPA Order 3336

11. CONTROLLING OFFICE NAME AND ADDRESS
Defense Advanced Research Projects Agency
1400 Wilson Boulevard
Arlington, VA 22209

12. REPORT DATE 11
31 December 1977

13. NUMBER OF PAGES
14

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Electronic Systems Division
Hanscom AFB
Bedford, MA 01731

12 13p.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

None

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

surface-relief structures
single-crystal films
reactive ion etching
holographic lithography
x-ray lithography
enhanced heteroepitaxy
thin film growth

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Oriented crystal growth on an amorphous substrate has been achieved using an artificially created submicrometer-dimension surface-relief grating. Crystallites of KCl grown from a water solution onto a 320-nm spatial-period square-wave grating in SiO_2 nucleated preferentially at vertical steps and grew with <100> directions parallel to the grating axis. 320-nm spatial-period square-wave gratings fabricated on amorphous SiO_2 substrates were used to produce uniform alignment of the director in nematic and smectic liquid-crystal layers. This demonstrates that molecular alignment can be achieved using surface structures fabricated by a planar process. A novel method of producing twisted-nematic liquid-crystal displays using surface gratings is described.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

207650

16